

Water-treated Rh/ γ -Al₂O₃ catalyst for methane partial oxidation

Xia Xu^{1,2} · Alan M. Lane^{1,2}

Received: 28 July 2015 / Accepted: 17 December 2015 / Published online: 3 February 2016
© The Author(s) 2016. This article is published with open access at Springerlink.com

Abstract A water treatment technique, using H₂ as a reducing agent in a wet environment, was applied to a conventional Rh/ γ -Al₂O₃ catalyst. Both standard- and water-treated Rh/ γ -Al₂O₃ catalysts were prepared and their catalytic performances were tested in methane partial oxidation reaction. The water-treated Rh/ γ -Al₂O₃ catalyst shows higher CO selectivity and lower CO₂ selectivity between 300 and 600 °C, compared with the standard-treated catalyst. The enhancement is attributed to the formation of well-dispersed smaller Rh nanoparticles.

Keywords Rh/ γ -Al₂O₃ catalyst · Methane partial oxidation · Water treatment

Introduction

Production of synthesis gas (H₂ and CO gas mixture) by methane (CH₄) partial oxidation (MPO) is an important intermediate step in many existing energy conversion technologies, such as fuel cells and Fischer–Tropsch reaction [1–5]. Decreasing the reaction temperature and improving the reaction efficiency have been a great challenge to researchers. One of the solutions is to develop high-efficiency catalysts. Our group in their previous research [6–8] showed that treating a Pt/ γ -Al₂O₃ catalyst at 500 °C in a humid reducing environment (H₂O/H₂) can

significantly decrease the reaction temperature of catalytic CO preferential oxidation in H₂. This is due to the decreased particle size, increased stability of Pt, and decreased CO chemisorption strength. In a subsequent research by others, a similar water treatment technique for reducing reaction temperature was also investigated and confirmed [9, 10].

In this work, we applied the same water treatment technique to Rh/ γ -Al₂O₃ catalysts and investigated its catalytic effects on the MPO reaction. The reaction products were analyzed by mass spectrometry (MS), and the catalyst morphology was characterized by transmission electron microscopy (TEM). The results show that water-treated Rh/ γ -Al₂O₃ catalyst can effectively decrease the size of Rh nanoparticles, and the water-treated Rh/ γ -Al₂O₃ catalyst shows higher CO selectivity in the temperature range of 300–600 °C.

Experiment

Catalyst preparation

Catalyst standard treatment

1 wt% Rh/ γ -Al₂O₃ catalyst was prepared by the incipient wetness method. Alumina (γ -Al₂O₃, 150 m²/g, acid type, ~0.25 mm, Alfa) was first calcined in air at 500 °C for 2 h to remove volatiles and then impregnated using an aqueous solution of Rh(NO₃)₂ (Alfa). The catalyst was dried in a fume hood overnight, followed by calcination in air at 500 °C for 2 h. The catalyst was finally reduced in H₂ at 500 °C for 2 h and cooled down with N₂ protection. This process is considered to be the standard treatment of the catalyst, as shown in Fig. 1.

✉ Alan M. Lane
alane@eng.ua.edu

¹ Center for Materials for Information Technology,
The University of Alabama, Tuscaloosa, AL 35487, USA

² Department of Chemical and Biological Engineering,
The University of Alabama, Tuscaloosa, AL 35487, USA

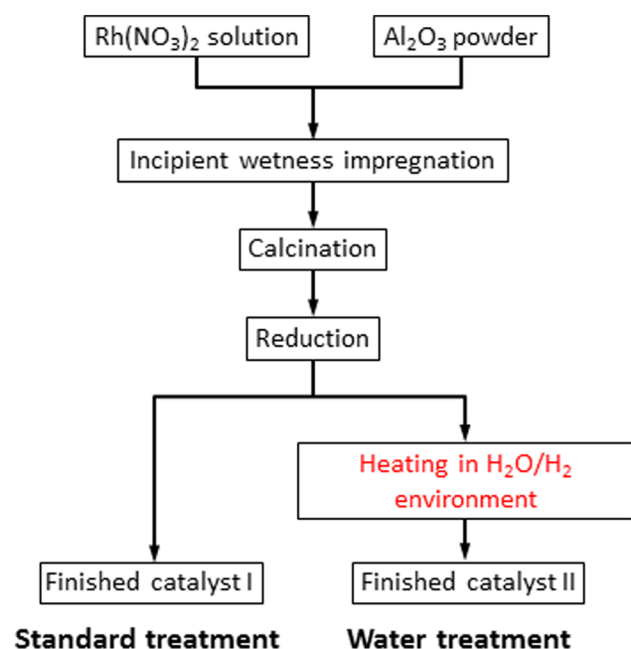


Fig. 1 Rh/ γ -Al₂O₃ catalyst preparation process: standard treatment and water treatment

Catalyst water treatment

Water treatment begins after the standard treatment of the catalyst. The standard-treated catalyst (0.1 g) was first wetted with 5 mL deionized (DI) water, then reduced in H₂ for 1 h at 500 °C at a heating rate of 10 °C/min, and finally cooled down to room temperature with N₂ protection. This process is considered to be the water treatment of the catalyst, as shown in Fig. 1. γ -Al₂O₃ can be potentially converted into hydrated boehmite (AlOOH) by reacting with water, and the acidity and surface area could be decreased. However, this reaction needs high temperature and pressure [11–13]. Overall, the water treatment process proposed in this study is safer to use in the case of γ -Al₂O₃.

Catalyst testing and characterization

Figure 2 shows a schematic of MPO system for testing the above catalysts. A Hiden Catlab Microreactor with a vertical quartz tube (6 mm I.D.) was used for the reaction. The gas flow rates were controlled by mass flow controllers (MFC), and the reaction temperature was controlled by a programmable controller. The catalyst (0.1 g) was fixed inside the vertical reactor with quartz fibers. The gas flow rates of CH₄, O₂, and Ar were controlled to 40, 20, and 20 ml/min, respectively. A mass spectrometer (Hiden QIC-20, MS) was used to analyze the reaction products, and Ar was used as an internal standard. A

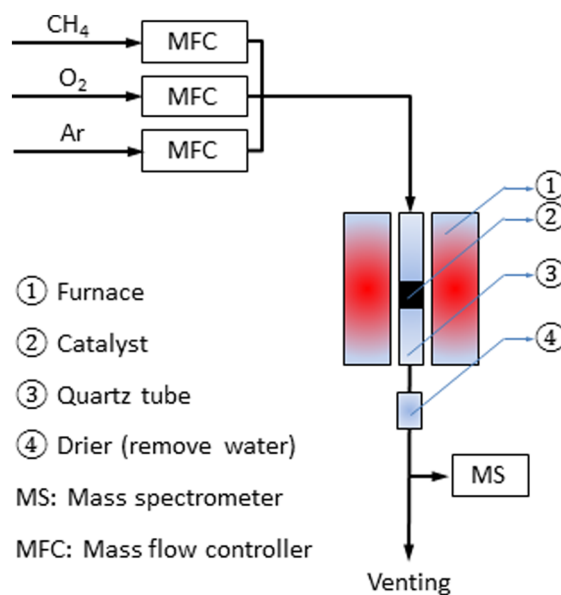


Fig. 2 A schematic of methane partial oxidation system

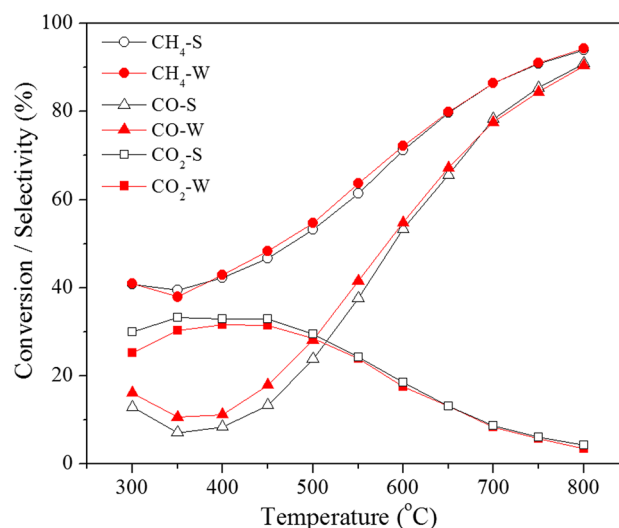


Fig. 3 The CH₄ conversion, CO and CO₂ selectivities of the standard-treated and water-treated 1 wt% Rh/ γ -Al₂O₃ catalysts in methane partial oxidation reaction (S standard-treated catalyst, W water-treated catalyst)

calcium sulfate (CaSO₄) as a dryer was located between reactor and MS to remove the water from the products and therefore to prevent plugging of the MS capillary tube by water. The test conditions adopted were between room temperature and 800 °C at 1 atm, and data were collected every 50 °C from 300 to 800 °C, as the ignition temperature of MPO with a Rh/ γ -Al₂O₃ catalyst is around 275 °C [14].

The conversion of CH₄ and the selectivities of CO and CO₂ were calculated using the following formulas:

$$\text{CH}_4 \text{ Conversion} : \frac{\text{CO}_{\text{out}} + \text{CO}_{2\text{out}}}{\text{CO}_{\text{out}} + \text{CO}_{2\text{out}} + \text{CH}_{4\text{out}}}; \quad (1)$$

$$\text{CO Selectivity} : \frac{\text{CO}_{\text{out}}}{\text{CO}_{\text{out}} + \text{CO}_{2\text{out}} + \text{CH}_{4\text{out}}}; \quad (2)$$

$$\text{CO}_2 \text{ Selectivity} : \frac{\text{CO}_{2\text{out}}}{\text{CO}_{\text{out}} + \text{CO}_{2\text{out}} + \text{CH}_{4\text{out}}}. \quad (3)$$

Transmission electron microscopy (TECNAI FEI 20, TEM) was used to characterize the size and morphology of the Rh nanoparticles on $\gamma\text{-Al}_2\text{O}_3$ support before the reaction. Each catalyst was ground in a mortar for 5 min and then dispersed in ethanol with ultrasonication. The dispersed particle was dropped onto a copper TEM grid with a carbon substrate and then dried for TEM characterization.

Results and discussion

Figure 3 shows the CH_4 conversion, CO and CO_2 selectivities of the standard-treated (“S”) and water-treated (“W”) Rh/ $\gamma\text{-Al}_2\text{O}_3$ catalysts in the MPO reaction. CH_4 conversion under both catalysts is similar in the temperature range of 300–800 °C. However, the water-treated catalyst shows higher CO selectivity and lower CO_2 selectivity than the standard-treated catalyst between 300 and 600 °C. The selectivities of CO and CO_2 of both catalysts are similar when the temperature is higher than 600 °C. This can be attributed to the MPO reaction reaching the thermodynamic equilibrium, and catalysts cannot change their reaction behavior. To confirm the

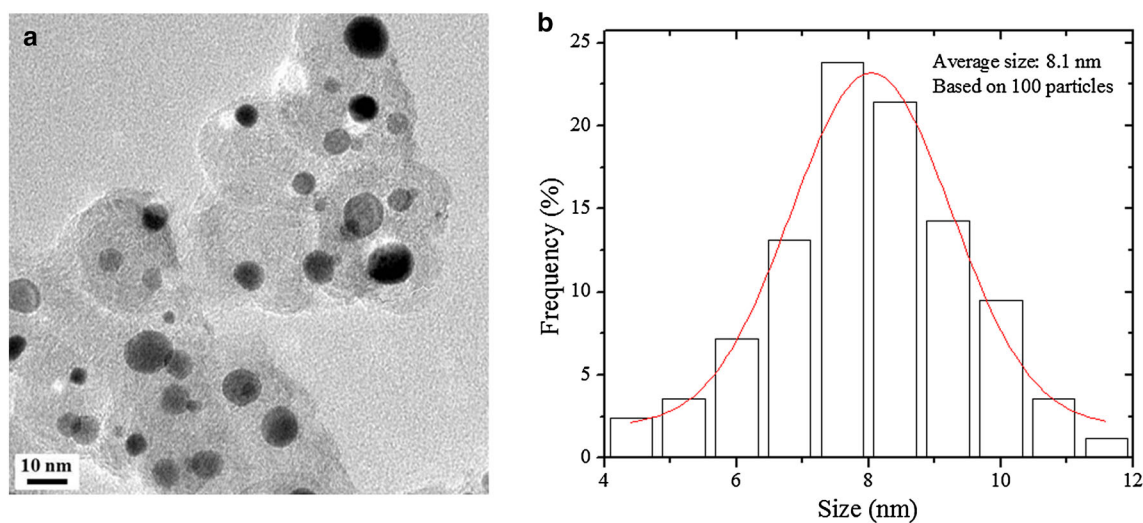


Fig. 4 Standard-treated 1 wt% Rh/ $\gamma\text{-Al}_2\text{O}_3$ catalyst: (a) TEM image; (b) Rh nanoparticle size distribution

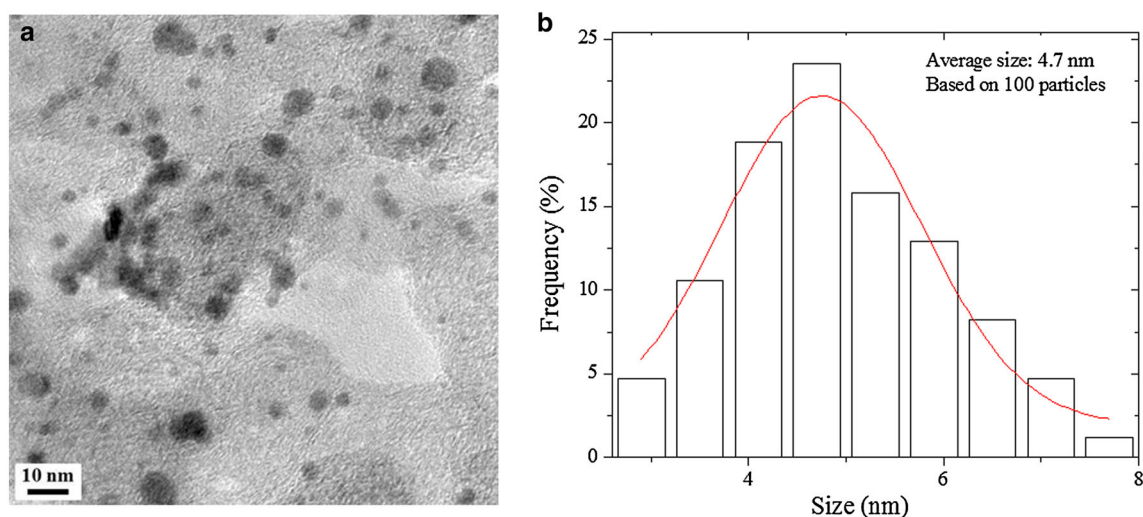


Fig. 5 Water-treated 1 wt% Rh/ $\gamma\text{-Al}_2\text{O}_3$ catalyst: (a) TEM image; (b) Rh nanoparticle size distribution

repeatability of this phenomena, the catalytic reactions were tested in different reaction cycles of the same catalyst and different batches of standard/water-treated catalysts, and the results were found to be consistent.

The TEM images of the standard-treated and water-treated catalysts are shown in Figs. 4a and 5a, respectively. The dark parts denote Rh nanoparticles and the brighter parts γ -Al₂O₃ particles, and Rh has higher electron density than Al because of larger atomic number. The average size of the Rh nanoparticles in the water-treated catalyst is 4.7 nm (Fig. 5b), much smaller than the standard-treated catalyst wherein the average size is 8.1 nm (Fig. 4b).

The increased selectivity of CO and the decreased selectivity of CO₂ of the water-treated catalyst could be attributed to smaller Rh nanoparticles on the alumina support, as they could provide larger surface areas and increase the contact area with reactants, thus providing higher CO selectivity. Unpublished results [15] for Pt/ γ -Al₂O₃ suggest that the chemisorption strength of CO on water-treated catalysts is significantly reduced, allowing more competitive adsorption of other reactants and products. These water treatment mechanisms require more investigation, but are thought to involve a type of metal-support interaction.

Conclusions

Both standard-treated and water-treated catalysts were tested for methane partial oxidation reaction. Water-treated catalyst shows higher CO and lower CO₂ selectivity in the temperature range of 300–600 °C. The enhancement is attributed to the formation of well-dispersed smaller Rh nanoparticles after water treatment. Further research is needed to explore the mechanism of Rh nanoparticle size decreasing during the water treatment process.

Acknowledgments This work was supported by the Department of Energy (DOE), Institute for Sustainable Energy, under the contract GR23134. This work utilized TEM owned and maintained by the Central Analytical Facility, which is supported by The University of Alabama.

Open Access This article is distributed under the terms of the Creative Commons Attribution 4.0 International License (<http://creativecommons.org/licenses/by/4.0/>), which permits unrestricted use, distribution, and reproduction in any medium, provided you give appropriate credit to the original author(s) and the source, provide a link to the Creative Commons license, and indicate if changes were made.

References

1. Khine MSS, Chen LW, Zhang S, Lin JY, Jiang SP (2013) Syngas production by catalytic partial oxidation of methane over (La_{0.7}A_{0.3})BO₃ (A = Ba, Ca, Mg, Sr, and B = Cr or Fe) perovskite oxides for portable fuel cell applications. *Int J Hydrog Energ* 38(30):13300–13308
2. Liso V, Olesen AC, Nielsen MP, Kaer SK (2011) Performance comparison between partial oxidation and methane steam reforming processes for solid oxide fuel cell (SOFC) micro combined heat and power (CHP) system. *Energy* 36(7):4216–4226
3. Pinol S, Morales M, Espiell F (2008) Hydrogen production by a new selective partial oxidation of methane in air using reduced La_{0.5}Sr_{0.5}CoO₃-delta as catalyst for fuel cell applications. *J New Mat Electr Syst* 11(2):119–124
4. Li B, Li H, Weng WZ, Zhang Q, Huang CJ, Wan HL (2013) Synthesis gas production from partial oxidation of methane over highly dispersed Pd/SiO₂ catalyst. *Fuel* 103:1032–1038
5. Dai XP, Yu CC (2009) Direct partial oxidation of methane to synthesis gas using oxygen carriers in the absence of gaseous oxygen. *Prog Chem* 21(7–8):1626–1635
6. Son IH, Shamsuzzoha M, Lane AM (2002) Promotion of Pt/gamma-Al₂O₃ by new pretreatment for low-temperature preferential oxidation of CO in H₂ for PEM fuel cells. *J Catal* 210(2):460–465
7. Jo MC, Kwon GH, Li W, Lane AM (2009) Preparation and characteristics of pretreated Pt/alumina catalysts for the preferential oxidation of carbon monoxide. *J Ind Eng Chem* 15(3):336–341
8. Son IH, Lane AM, Johnson DT (2003) The study of the deactivation of water-pretreated Pt/gamma-Al₂O₃ for low-temperature selective CO oxidation in hydrogen. *J Power Sources* 124(2):415–419
9. Tomita A, Shimizu K, Kato K, Akita T, Tai Y (2013) Mechanism of low-temperature CO oxidation on Pt/Fe-containing alumina catalysts pretreated with water. *J Phys Chem C* 117(3):1268–1277
10. Tomita A, Shimizu K, Kato K, Tai Y (2012) Pt/Fe-containing alumina catalysts prepared and treated with water under moderate conditions exhibit low-temperature CO oxidation activity. *Catal Commun* 17:194–199
11. Ketchie WC, Maris EP, Davis RJ (2007) In-situ X-ray absorption spectroscopy of supported Ru catalysts in the aqueous phase. *Chem Mater* 19(14):3406–3411
12. Ravenelle RM, Copeland JR, Kim WG, Crittenden JC, Sievers C (2011) Structural changes of gamma-Al₂O₃-supported catalysts in hot liquid water. *ACS Catal* 1(5):552–561
13. Luo NJ, Fu XW, Cao FH, Xiao TC, Edwards PP (2008) Glycerol aqueous phase reforming for hydrogen generation over Pt catalyst: effect of catalyst composition and reaction conditions. *Fuel* 87(17–18):3483–3489
14. Lopez-Fonseca R, Jimenez-Gonzalez C, de Rivas B, Gutierrez-Ortiz JI (2012) Partial oxidation of methane to syngas on bulk NiAl₂O₄ catalyst. Comparison with alumina supported nickel, platinum and rhodium catalysts. *Appl Catal A-Gen* 437:53–62
15. Son, IH (2003) Promotion of Platinum/gamma-aluminum oxide for preferential oxidation of carbon monoxide in hydrogen for PEM fuel cells by cerium promoter and by preparation of stable platinum nanoparticles using a water-pretreatment. Ph.D. Dissertation, the University of Alabama